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Formation of a Dirhenium Carbene Complex from Reaction of (η^5-C_5H_4Li)$Re(CO)_3$ with (η^5-C_5H_5)$Re(CO)_3$

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The ring-metalated complex (η^5-C_5H_4Li)$Re(CO)_3$ generated by reaction of (η^5-C_5H_5)$Re(CO)_3$ with *n*-BuLi in THF at −78 °C reacted with additional (η^5-C_5H_5)$Re(CO)_3$ to produce the dirhenium acyl anion (η^5-C_5H_5)$(CO)_2Re(C{=}O)[(\eta^5\text{-}C_5H_4)Re(CO)_3]^-Li^+$. Protonation of this acyl anion gave the dirhenium hydroxycarbene complex (η^5-C_5H_5)$(CO)_2Re{=}C(OH)[(\eta^5\text{-}C_5H_4)\text{-}Re(CO)_3]$, while methylation gave the methoxycarbene complex (η^5-C_5H_5)$(CO)_2Re{=}C(OCH_3)\text{-}[(\eta^5\text{-}C_5H_4)Re(CO)_3]$, which was characterized by X-ray crystallography. The methoxycarbene complex reacted with *n*-BuLi to produce the butylcarbene complex (η^5-C_5H_5)$(CO)_2Re{=}C\text{-}(CH_2CH_2CH_2CH_3)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$.

Introduction

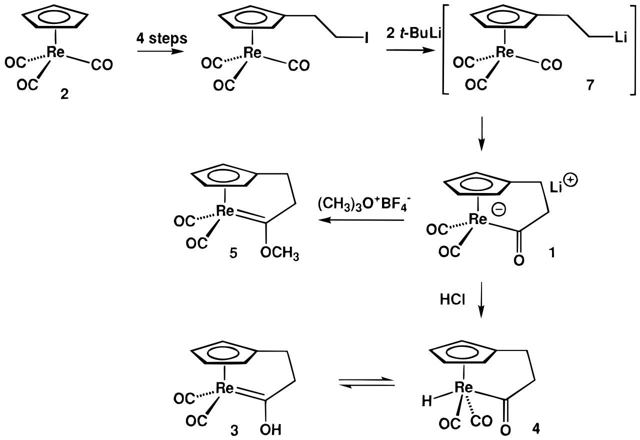
Recently we reported a five-step synthesis of the tethered acyl anion $[(CO)_2Re(C{=}O)CH_2CH_2(\eta^5\text{-}C_5H_4)]^-Li^+$ (**1**) from (η^5-C_5H_5)$Re(CO)_3$ (**2**) (Scheme 1).[1] Protonation of this anion gave an equilibrium mixture of hydroxycarbene complex $(CO)_2Re{=}C(OH)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**3**) and the isomeric acyl hydride *trans*-$H(CO)_2Re(C{=}O)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**4**). Methylation of anion **1** with $(CH_3)_3O^+BF_4^-$ gave the methoxycarbene complex $(CO)_2Re{=}C(OCH_3)CH_2CH_2(\eta^5\text{-}C_5H_4)$ (**5**), while methylation with CH_3I produced the methyl acyl complex *trans*-$CH_3(CO)_2Re(C{=}O)CH_2CH_2(\eta^5\text{-}C_5H_4)$.

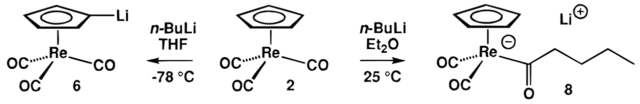
In an attempt to develop a shorter and more efficient synthesis of **1**, we initiated a study of the reaction of the ring-metalated anion (η^5-C_5H_4Li)$Re(CO)_3$ (**6**) with ethylene as an alternative route to $((\eta^5\text{-}C_5H_4)CH_2CH_2\text{-}Li)Re(CO)_3$ (**7**). Here we report that, instead of reacting with ethylene to eventually form **1**, the ring-metalated anion **6** reacts with a carbonyl ligand of (η^5-C_5H_5)$Re(CO)_3$ (**2**).

Results and Discussion

Chemoselectivity of Reaction of *n*-BuLi with (η^5-C_5H_5)$Re(CO)_3$ (2). The reaction of **2** with *n*-BuLi is strongly solvent and temperature dependent. Fischer reported that *n*-BuLi in Et_2O at room temperature adds to a carbonyl ligand of **2** to give the acyl anion $[(\eta^5\text{-}C_5H_5)(CO)_2Re(C{=}O)CH_2CH_2CH_2CH_3]^-Li^+$ (**8**), which was then converted to $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OCH_3)CH_2CH_2\text{-}CH_2CH_3$ (**9**) in 8% overall yield.[2] In contrast, Nesmeyanov reported that *n*-BuLi in THF at low temperature ring-metalates **2** to give **6**, which reacts with CO_2 to give $((\eta^5\text{-}C_5H_4)CO_2H)Re(CO)_3$ in 93% overall yield after hydrolysis.[3] To determine whether the change in chemoselectivity is a solvent or temperature effect, we have studied the reactions of *n*-BuLi with **2** in more detail.

Scheme 1





In *Et_2O* at −78 °C, there is no reaction between *n*-BuLi and **2**. For example, when *n*-BuLi was added to **2** in Et_2O at −78 °C and then quenched with CD_3OD at −78 °C after 3 h, **2** was recovered unchanged in 100% yield, and mass spectral analysis showed <1% (η^5-C_5H_4D)$Re(CO)_3$. Similarly, when *n*-BuLi was added to **2** in Et_2O at −78 °C and then quenched with CH_3I at −78 °C after 3 h, **2** was recovered unchanged in 84% yield, and ^1H NMR analysis showed no formation of the known (η^5-$C_5H_4CH_3$)$Re(CO)_3$ (**10**).[4] We confirmed that reaction of **2** with *n*-BuLi at room temperature in Et_2O produced the acyl anion **8**, which was converted to butylmethoxycarbene complex **9** in 17% isolated yield.

In contrast, in *THF* at −78 °C, reaction of **2** with *n*-BuLi for 3 h followed by quenching with CD_3OD at −78 °C gave (η^5-C_5H_4D)$Re(CO)_3$, which was isolated in 94% yield and was shown by mass spectral analysis to be 75% d_1. Similarly, reaction of **2** with *n*-BuLi in

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S0276-7333(96)00448-7 CCC: $12.00

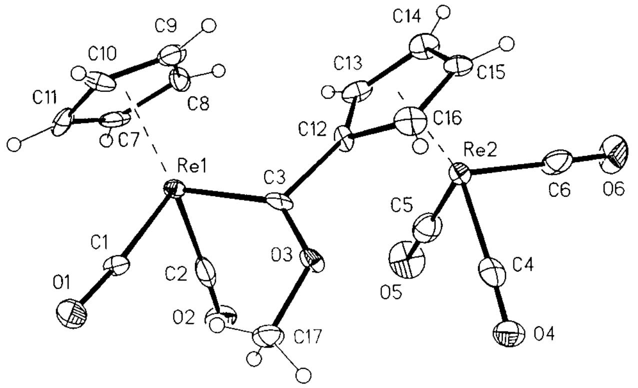
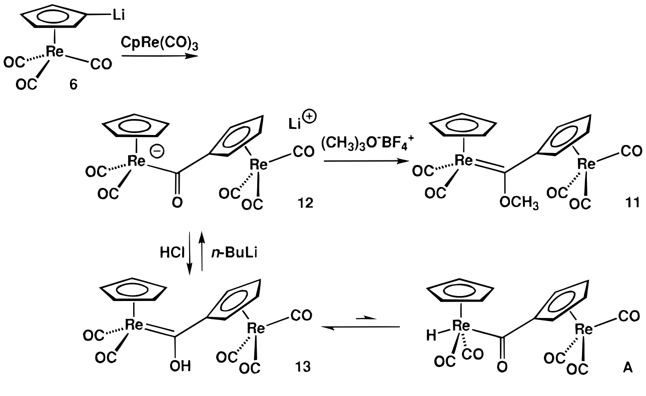


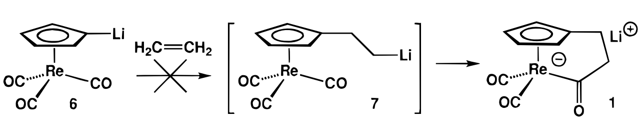
Figure 1. Structure of (η^5-C_5H_5)(CO)$_2$Re=C(OCH$_3$)[(η^5-C_5H_4)Re(CO)$_3$] (**11**).

Scheme 2



THF at −78 °C followed by quenching with CH_3I at −78 °C after 3 h gave (η^5-$C_5H_4CH_3$)Re(CO)$_3$ (**10**) in 84% isolated yield with no (η^5-C_5H_5)Re(CO)$_3$ observed. While the greater reactivity of *n*-BuLi in THF compared to that in Et_2O is well precedented, we do not understand the observed solvent dependence of chemoselectivity.

Attempted Reaction of Ethylene with (η^5-C_5H_4Li)-Re(CO)$_3$ (6). In an attempt to develop a shorter synthesis of tethered anion **1**, we studied the reaction of **6** with ethylene. Additions of carbanions to ethylene, styrene, isobutylene, and propene are known.[5]



Ring-metalated anion **6** was generated by treating **2** with *n*-BuLi in THF at −78 °C. After 3 h, ethylene was condensed into the solution at −78 °C in an effort to generate (η^5-$C_5H_4CH_2CH_2Li$)Re(CO)$_3$ (**7**). The solution was warmed to room temperature, and $(CH_3)_3O^+BF_4^-$ was added. Earlier we showed that **7** forms tethered anion **1**, which reacts with $(CH_3)_3O^+BF_4^-$ to give the methoxycarbene complex **5**.[1] However, no **5** was detected in the reaction mixture. Instead, the dinuclear methoxycarbene complex (η^5-C_5H_5)(CO)$_2$Re=C(OCH$_3$)-[(η^5-C_5H_4)Re(CO)$_3$] (**11**) was isolated by thin-layer chromatography as an orange solid in 13% yield.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (η^5-C_5H_5)(CO)$_2$Re=C(OCH$_3$)[(η^5-C_5H_4)Re(CO)$_3$] (11)

Bond Distances			
Re1−C1	1.876(13)	C3−C12	1.52(2)
Re1−C2	1.93(2)	Re2−C4	1.91(2)
Re1−C2	1.93(2)	Re2−C5	1.92(2)
Re1−C3	2.025(12)	Re2−C6	1.93(2)
C1−O1	1.16(2)	C4−O4	1.14(2)
C2−O2	1.16(2)	C5−O5	1.16(2)
C3−O3	1.30(2)	C6−O6	1.15(2)
C3−C17	1.43(2)		
Bond Angles			
C1−Re1−C2	86.1(6)	C3−O3−C17	121.7(9)
C1−Re1−C3	95.9(5)	C3−C12−C13	129.0(11)
C2−Re1−C3	87.7(5)	C3−C12−C16	124.9(11)
$Cp_{cent\ 1}$−Re1−C3	126.3	C3−C12−$Cp_{cent\ 2}$	183.7
Re1−C3−O3	133.1(9)	C4−Re2−C5	87.8(6)
Re1−C3−C12	121.8(9)	C4−Re2−C6	90.6(6)
C12−C3−O3	105.1(9)	C5−Re2−C6	89.7(7)

Characterization of the Dinuclear Carbene Complex (η^5-C_5H_5)(CO)$_2$Re=C(OCH$_3$)[(η^5-C_5H_4)Re(CO)$_3$] (11). A single-crystal X-ray crystallographic study of the orange solid established the structure of the dinuclear carbene complex **11** (Figure 1, Table 1). Unlike the strained tethered methoxycarbene complex **5**, dirhenium complex **11** is unstrained. The $Cp_{cent\ 1}$−Re1−C3 angle of 126.3° is that expected for a normal three-legged piano-stool complex. The carbene carbon atom is nearly coplanar with the cyclopentadienyl ligand ($Cp_{cent\ 2}$−C12−C3 = 183.7°), as expected for cyclopentadienyl substituents in an unstrained complex.[6] The Re1−C3 distance of 2.025 Å is slightly longer than other rhenium-carbon double bonds.[7]

Key spectral features of **11** include four metal carbonyl bands in the IR spectrum. Two bands of similar intensity at 1957 and 1881 cm^{-1} are assigned to the carbonyl ligands of the Re(CO)$_2$ unit of the molecule, on the basis of similarities to (η^5-C_5H_5)(CO)$_2$Re=C-(OCH$_3$)C_6H_5 and (η^5-C_5H_5)(CO)$_2$Re=C(OCH$_3$)CH_2CH_2-CH_2CH_3.[2] Bands at 2024 and 1929 cm^{-1} are assigned to the carbonyl ligands of the Re(CO)$_3$ unit of **11** on the basis of similarities to CpRe(CO)$_3$. The ^{1}H NMR spectrum of **11** in acetone-d_6 shows a cyclopentadienyl singlet at δ 5.59 and an AA′BB′ pattern for cyclopentadienyl resonances of the substituted ring, with virtual triplets at δ 5.82 and 5.53. The ^{13}C NMR spectrum of **11** in CD_2Cl_2 shows the carbene carbon resonance characteristically downfield at δ 271.2.[8] Separate carbonyl resonances are observed at δ 202.7 for the dicarbonyl portion and at δ 194.2 for the tricarbonyl portion of the molecule. Cyclopentadienyl resonances were observed at δ 94.9 (C_5H_4, ipso), 88.4 (C_5H_5), 85.4 (C_5H_4), and 83.4 (C_5H_4).

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When excess CpRe(CO)$_3$ (**2**) was added to a preformed light yellow solution of ring-metalated **6** at −78 °C, no color change occurred until the solution was warmed to about −20 °C. Then the solution became red-orange, the color of the isolated acyl anion [(η^5-C$_5$H$_5$)(CO)$_2$Re=C(O)[(η^5-C$_5$H$_4$)Re(CO)$_3$]$^-$Li$^+$ (**12**) (see below). Addition of (CH$_3$)$_3$O$^+$BF$_4^-$ led to the isolation of dinuclear carbene complex **11** in 43% yield.

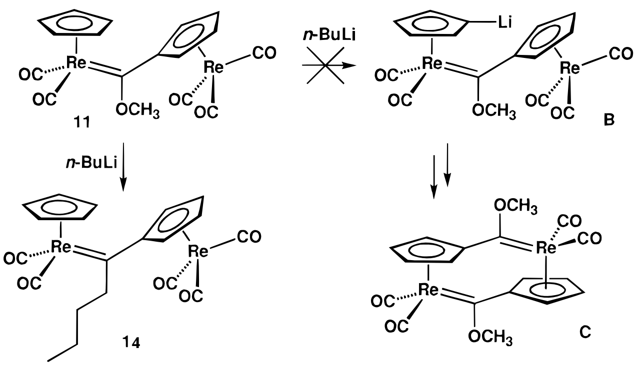
The formation of **11** is readily explained by initially relatively rapid ring metalation of **2** to give **6**, which then reacts more slowly with **2** to give the binuclear acyl anion **12** (Scheme 2). This is consistent with the higher yield of **11** obtained from reaction of preformed **6** with excess **2**. When **6** was generated in the presence of ethylene and then warmed to room temperature, apparently adventitious partial hydrolysis of **6** regenerated some **2**, which then reacted with **6** to eventually give a low yield of **11**.

The proposed acyl anion **12** was isolated by addition of **2** to **6** in THF at −78 °C followed by evaporation of solvent at room temperature. The anion was characterized spectroscopically. The IR spectrum of **12** in THF showed two bands at 1917 and 1828 cm^{-1} assigned to carbonyl ligands of the anionic Re(CO)$_2$ center and two bands at 1998 and 1895 cm^{-1} assigned to the Re(CO)$_3$ unit. The ^{1}H NMR spectrum in THF-d_8 showed a cyclopentadienyl singlet at δ 5.49 for the unsubstituted ring and virtual triplets at δ 5.73 and 5.27 for the four cyclopentadienyl protons of the substituted ring. The ^{13}C NMR spectrum in THF-d_8 showed an acyl carbon resonance at δ 255.6 and separate resonances for carbonyl ligands of the dicarbonyl and tricarbonyl units of the molecule at δ 209.0 and 196.2, respectively.

The Dinuclear Hydroxycarbene Complex (η^5-C$_5$H$_5$)(CO)$_2$Re=C(OH)[(η^5-C$_5$H$_4$)Re(CO)$_3$] (13). Addition of aqueous HCl to a CH$_2$Cl$_2$ suspension of the anion **12** followed by extraction of the organic phase led to the isolation of dirhenium hydroxycarbene complex (η^5-C$_5$H$_5$)(CO)$_2$Re=C(OH)[(η^5-C$_5$H$_4$)Re(CO)$_3$] (**13**) (Scheme 2). Treatment of **13** with *n*-BuLi regenerated **12**. The IR spectrum of **13** consisted of two equal-intensity bands at 1960 and 1889 cm^{-1} assigned to the Re(CO)$_2$ unit and a strong band at 2026 cm^{-1} and a very strong band at 1933 cm^{-1} assigned to the Re(CO)$_3$ unit of **13**. The OH stretch was observed as a broad weak band centered at 3164 cm^{-1}. The ^{1}H NMR spectrum in acetone-d_6 showed a broad hydroxyl resonance centered at δ 11.76. None of the isomeric acyl hydride (η^5-C$_5$H$_5$)(CO)$_2$(H)Re(C=O)[(η^5-C$_5$H$_4$)Re(CO)$_3$] (**A**) was detected. Even in CD$_2$Cl$_2$, a solvent which favored acyl hydride **4** in the equilibrium mixture of **3** and **4**, no resonances appeared in the hydride region (δ 0 to −10) of the expanded spectrum, and **13** was the only compound observed. The only time we have observed an acyl hydride in equilibrium with a hydroxycarbene complex was in the case of **3** and **4**, where the hydroxycarbene tautomer was destabilized by the strain of the two-carbon tether.

Reaction of *n*-BuLi with the Dinuclear Carbene Complex (η^5-C$_5$H$_5$)(CO)$_2$Re=C(OCH$_3$)[(η^5-C$_5$H$_4$)Re(CO)$_3$] (11). The reaction of **11** with *n*-BuLi was studied in the hope that ring metalation might occur on the unsubstituted Cp ring and that the resulting lithium reagent generated might attack a carbonyl ligand on the neighboring center (Scheme 3). After methylation this might have produced the cyclic symmetric bis(carbene) complex (η^5-C$_5$H$_4$)(CO)$_2$Re=C(OCH$_3$)[(η^5-C$_5$H$_4$)Re=C(OCH$_3$)(CO)$_2$] (**C**). However, *n*-BuLi simply added to the carbene carbon of **11**. After workup with acid, the butylcarbene complex (η^5-C$_5$H$_5$)(CO)$_2$Re=C(CH$_2$CH$_2$CH$_2$CH$_3$)[(η^5-C$_5$H$_4$)Re(CO)$_3$] (**14**) was obtained in 15% isolated yield. The ^{1}H NMR spectrum of **14** shows a cyclopentadienyl singlet at δ 5.88 and virtual triplets for the protons of the substituted ring at δ 6.10 and 5.72. The butyl chain gives rise to an AA′BB′ pattern at δ 3.05, multiplets at δ 1.70 and 1.50, and a triplet at δ 0.94. The addition of nucleophiles to carbene complexes in this manner is well-known.[9]

Scheme 3



Experimental Section

General Methods. All manipulations were performed under a nitrogen atmosphere in an inert-atmosphere glovebox or by standard high-vacuum-line techniques. ^{1}H NMR spectra were obtained on a Bruker WP200 or AM300 spectrometer, and ^{13}C NMR spectra were obtained on a Bruker AM500 (125 MHz) spectrometer. Infrared spectra were recorded on a Mattson Genesis FT-IR spectrometer. Mass spectra were determined on a Kratos MS-80 spectrometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Diethyl ether, THF, and hexane were distilled from sodium and benzophenone; methylene chloride was distilled from CaH$_2$. THF-d_8 and C$_6$D$_6$ were distilled from sodium and benzophenone; acetone-d_6 was distilled from B$_2$O$_3$; CD$_2$Cl$_2$ was distilled from P$_2$O$_5$. *n*-BuLi and (CH$_3$)$_3$OBF$_4$ were used as received from Aldrich.

(η^5-C$_5$H$_5$)(CO)$_2$Re=C(OCH$_3$)CH$_2$CH$_2$CH$_2$CH$_3$ (9). The synthesis of **9** was repeated according to the method reported by Fischer,[2] except that anion **8** was methylated with (CH$_3$)$_3$O$^+$BF$_4^-$ instead of acid and diazomethane. *n*-BuLi (0.4 mL, 1.5 M solution in hexane) was added to a solution of (η^5-C$_5$H$_5$)Re(CO)$_3$ (200 mg, 0.60 mmol) in Et$_2$O (10 mL) at −78 °C, and the solution was warmed to 25 °C. After 3 h, solvent was evaporated and the orange residue was treated with (CH$_3$)$_3$O$^+$BF$_4^-$ (90 mg, 0.600 mmol) in acetone (10 mL) overnight. Thin-layer chromatography (SiO$_2$, 1:1 Et$_2$O−hexane) gave a yellow band (R_f = 0.9) from which **9** was isolated as a yellow oil (40 mg, 17%). ^{1}H NMR (acetone-d_6, 300 MHz): δ 5.24 (s, C$_5$H$_5$), 4.15 (s, OCH$_3$), 2.70 (AA′BB′, 17 Hz separation of outer lines, Re=CC*H*$_2$), 1.77 (multiplet, Re=CCH$_2$C*H*$_2$), 1.67

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(multiplet, CH_2CH_3), 0.89 (t, $J = 7.3$ Hz, CH_2CH_3). IR (THF): 1954 (s), 1879 (s) cm^{-1}.

$(\eta^5\text{-}C_5H_5)(CO)_2Re(C{=}O)[(\eta^5\text{-}C_5H_4)Re(CO)_3]^-Li^+$ (12). *n*-BuLi (0.4 mL, 1.5 M solution in hexane) was added to a solution of (η^5-C_5H_5)Re(CO)$_3$ (200 mg, 0.60 mmol) in THF (20 mL) at −78 °C. After 2 h, a solution of (η^5-C_5H_5)Re(CO)$_3$ (200 mg, 0.60 mmol) in THF (10 mL) was added. The solution was stirred overnight at room temperature, and THF was evaporated to give **12** as a red-orange powder (258 mg, 68%) which was shown to contain ~0.3 mol of Et_2O/mol of **12**. ^{1}H NMR (THF-d_8, 300 MHz) δ 5.73 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4), 5.49 (s, C_5H_5), 5.27 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4). ^{13}C NMR (THF-d_8, 126 MHz): δ 255.6 (Re=C), 209.0 (2 CO), 196.2 (3 CO), 86.6 (C_5H_5), 84.8 (C_5H_4, ipso), 85.8 (C_5H_4), 83.6 (C_5H_4). IR (THF): 1998 (m) (ν_{sym}(Re(CO)$_3$)), 1917 (s) (ν_{sym}(Re(CO)$_2$)), 1895 (s) (ν_{asym}(Re(CO)$_3$)), 1828 (m) (ν_{asym}(Re(CO)$_2$)) cm^{-1}.

$(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OCH_3)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$ (11). An orange solution of **12** (260 mg, 0.38 mmol) and $(CH_3)_3O^+BF_4^-$ (56 mg, 0.38 mmol) in acetone was stirred overnight. Solvent was evaporated, and the orange residue was dissolved in CH_2Cl_2 and filtered through celite. Preparative thin-layer chromatography (silica gel, 1:1 hexane−Et_2O) gave **11** ($R_f = 0.6$) as an orange solid (113 mg, 43%). Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of hexane into a saturated Et_2O solution. ^{1}H NMR (acetone-d_6, 300 MHz): δ 5.82 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4), 5.59 (s, C_5H_5), 5.53 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4), 4.18 (s, OCH_3). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 271.2 (Re=C), 202.7 (2 CO), 194.2 (3 CO), 94.9 (C_5H_4, ipso), 88.4 (C_5H_5), 85.4 (C_5H_4), 83.4 (C_5H_4). IR (THF): 2024 (m) (ν_{sym}(Re(CO)$_3$)), 1957 (m) (ν_{sym}(Re(CO)$_2$)), 1929 (s) (ν_{asym}(Re(CO)$_3$)), 1881 (m) (ν_{asym}(Re(CO)$_2$)) cm^{-1}. HRMS: calcd for $C_{17}H_{12}Re_2O_6$, 685.976; found, 685.980. Anal. Calcd (found) for $C_{17}H_{12}Re_2O_6$: C, 29.82 (29.93); H, 1.77 (1.84).

X-ray Crystallographic Determination and Refinement. Slow diffusion of hexane into a saturated solution of **11** in Et_2O in an inert-atmosphere glovebox gave orange crystals of **11** suitable for X-ray analysis. Intensity data were obtained with graphite-monochromated Mo Kα radiation on a Siemens P4 diffractometer at −125 °C. Crystallographic computations were carried out with SHELXTL and SHELXL−93.[10] A semiempirical absorption correction was applied. The initial positions of the Re atoms were obtained by automatic Patterson interpretation. Other non-hydrogen atoms were obtained from successive Fourier difference maps coupled with isotropic least-squares refinement. All non-hydrogen atoms were refined anisotropically. Idealized positions were used for the hydrogen atoms. Crystallographic data are presented in Table 2. Atomic coordinates and equivalent isotropic displacement parameters and a complete list of bond lengths and angles are presented in the Supporting Information.

$(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OH)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$ (13). Aqueous HCl (1 mL, 10 M, 10 mmol) was added to **11** (200 mg, 0.30 mmol) in a biphasic mixture of 10 mL of CH_2Cl_2 and 10 mL of H_2O. After rapid stirring for 10 min the CH_2Cl_2 layer was separated, washed with water, dried ($MgSO_4$), filtered, and concentrated to give a red residue. Thin-layer chromatography (Et_2O, silica gel) gave **13** ($R_f = 0.2$) as an orange liquid (85 mg, 42%). ^{1}H NMR (acetone-d_6, 300 MHz): δ 11.76 (s, OH), 6.10 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4), 5.68 (s, C_5H_5), 5.63 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4). ^{13}C NMR (C_6D_6, 126 MHz): δ 261.2 (Re=C), 203.7 (2 CO), 194.1 (3 CO), 113.1 (C_5H_4, ipso), 90.0 (C_5H_5), 88.5 (C_5H_4), 84.4 (C_5H_4). IR (THF): 3164 (br, w, ν_{OH}), 2026 (m) (ν_{sym}(Re(CO)$_3$)), 1960 (m) (ν_{sym}(Re(CO)$_2$)), 1933 (s) (ν_{asym}(Re(CO)$_3$)), 1889 (m) (ν_{asym}(Re(CO)$_2$)) cm^{-1}. HRMS: calcd for $C_{16}H_{10}Re_2O_6$, 669.957; found, 669.948.

Table 2. Crystal Structure Data for $(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(OCH_3)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$ (11)

empirical formula	$C_{17}H_{12}O_6Re_2$
color, habit	orange needle
cryst size	0.5 × 0.2 × 0.05 mm
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	$a = 7.1945(12)$ Å $b = 11.663(2)$ Å $c = 19.701(3)$ Å
V	1653.1 Å^3
2θ range of data collectn	3.0, 45
Z	4
fw	684.67
density (calcd)	2.751 g cm^{-3}
abs coeff	14.663 mm^{-1}
F(000)	1248
$R(F)$	3.19%
R_w $(F)^2$	8.03%

$(\eta^5\text{-}C_5H_5)(CO)_2Re{=}C(CH_2CH_2CH_2CH_3)[(\eta^5\text{-}C_5H_4)Re(CO)_3]$ (14). *n*-BuLi (0.10 mL, 1.5 M, 0.15 mmol) was added to **11** (90 mg, 0.13 mmol) in THF (10 mL) at −78 °C. After 2 h, anhydrous HCl (0.15 mmol) was condensed into the solution at −78 °C. The solution was stirred for 2 h at 25 °C. Thin-layer chromatography gave **13** ($R_f = 0.8$) as an orange solid (28 mg, 31%). ^{1}H NMR (acetone-d_6, 300 MHz): δ 6.10 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4), 5.88 (s, C_5H_5), 5.72 (AA′BB′ three-line pattern, 4.7 Hz separation of outer lines, C_5H_4), 3.05 (AA′BB′ pattern, Re=CCH_2), 1.70 (multiplet, Re=CCH_2CH_2), 1.50 (sextet, $J = 7.4$ Hz, CH_2CH_3), 0.94 (t, $J = 7.4$ Hz, CH_3). ^{13}C NMR (CD_2Cl_2, 126 MHz): δ 288.6 (Re=C), 205.2 (2 CO), 193.6 (3 CO), 124.9 (C_5H_4, ipso), 92.3 (C_5H_5), 85.0 (C_5H_4), 84.8 (C_5H_4), 63.0 (Re=CCH_2), 36.2 (Re=CCH_2CH_2), 23.1 (CH_2CH_3), 13.6 (CH_3). IR (THF): 2023 (m) (ν_{sym}(Re(CO)$_3$)), 1957 (m) (ν_{sym}(Re(CO)$_2$)), 1930 (s) (ν_{asym}(Re(CO)$_3$)), 1884 (m) (ν_{asym}(Re(CO)$_2$)) cm^{-1}. HRMS: calcd for $C_{20}H_{18}Re_2O_5$, 710.025; found, 710.024.

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Supporting Information Available: Tables giving X-ray crystallographic data for **11** (8 pages). Ordering information is given on any current masthead page.

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[10] Sheldrick, G. M. *SHELXTL Version 5 Reference Manual*, Siemens Analytical X-ray Instruments: Madison, WI, 1994.